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(54) TREATMENT OF CHROMIUM OXIDE AND SUB-BASE MATERIAL, LAND-FILLING MATERIAL AND TEMPORARY MATERIAL USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a process for treating chromium oxide containing substance-s that can inhibit the elution of Cr6+ from chromium oxide-containing substance, as stainless steel slag occurring in the refining of stainless steel, chromium slag occurring in the production of chromium compounds as sodium dichromate, molten slag of industrial waste, sewage sludge or refractory contaminated with slag used in the refining of stainless steel and provide the sub-base material, land-filling material and temporary material using the same. SOLUTION: In this treatment of chromium oxide-containing substance, 100 pts.wt. of a reductively treated chromium oxide-containing substance is mixed with 0.1-90 pts.wt. of sulfur. The sub-base material, land-filling material or temporary material is prepared by adding 0.1-90 pts.wt. of sulfur containing slag to 100 pts.wt. of the reductively treated chromium oxide-containing substance and mixing them.

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CLAIMS

[Claim(s)]

[Claim 1]Quality 100 of a chromium oxidation thing inclusion after reduction processing A disposal method of quality of a chromium oxidation thing inclusion 0.1---90-weight-section-adding sulfur content slag, and mixing to a weight section.

[Claim 2]Quality 100 of a chromium oxidation thing inclusion after reduction processing A utilizing method of quality of a chromium oxidation thing inclusion characterized for an obtained mixture by a thing of a roadbed material, engineering-works reclamation material, and temporary material used for either at least after 0.1---90-weight-section-adding sulfur content slag and mixing to a weight section.

[Claim 3]Quality 100 of a chromium oxidation thing inclusion after reduction processing A roadbed material characterized by being 0.1---90-weight-section-added and coming to mix sulfur content slag to a weight section.

[Claim 4]Quality 100 of a chromium oxidation thing inclusion after reduction processing Engineering-works reclamation material characterized by being 0.1---90-weight-section-added and coming to mix sulfur content slag to a weight section.

[Claim 5]Quality 100 of a chromium oxidation thing inclusion after reduction processing Temporary material characterized by being 0.1---90-weight-section-added and coming to mix sulfur content slag to a weight section.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]The stainless steel slag which generates this invention in the case of refinement of stainless steel, The chromium-ores slag by which it is generated in the case of manufacture of chromium compounds, such as potassium sodium, Industrial waste molten slag, The disposal method of the quality of a chromium oxidation thing inclusion which can prevent elution of Cr6+ from quality of a chromium oxidation thing inclusion, such as slag adherence refractories used for refinement of a sewage sludge and stainless steel, the utilizing method of the quality of a chromium oxidation thing inclusion using it and a roadbed material, engineering-works reclamation material, It is related with temporary material.

[0002]

[Description of the Prior Art]Generally, steelmaking slag is reused mainly as a roadbed material, engineering-works reclamation material, etc., after carrying out aging processing. Since the chromium oxidation thing of several percent is usually contained in the stainless steel slag generated in it in the case of stainless steel refinement, depending on the operating condition of refinement, the part oxidizes even to Cr6+.

[0003]For this reason, Cr6+ might elute with the minute amount at the time of reuse of slag, and it was one of the causes of concern at the time of slag reuse. The chromium-ores slag by which it is generated in the case of manufacture of chromium compounds, such as potassium sodium, Also when quality of a chromium oxidation thing inclusion, such as industrial waste molten slag (:Cr content slag) and a sewage sludge, was reused, Cr6+ might elute with the minute amount

like the above, and it was set to one of the causes of concern at the time of reusing these.

[0004] Then, when reusing these as a roadbed material, engineering-works reclamation material, etc., the new technology for preventing elution of Cr6+ is proposed. Namely, the stainless steel slag generated in the case of refinement of stainless steel, It is following (1) as an elution prevention method of Cr6+ from quality of a chromium oxidation thing inclusion, such as chromium-ores slag, a sewage sludge, etc. by which it is generated in the case of manufacture of chromium compounds, such as potassium sodium. The technology of - (4) is indicated.

[0005] (1) An elution prevention method of Cr6+ from the stainless steel slag which adds aluminum ash and magnesia system industrial waste to stainless steel slag (JP,H6-171993,A).

(2) As opposed to the slag of the molten state which passed through the reduction processing which collects Cr(s) after decarbonization refinement of stainless steel, and in slag into molten steel, How (JP,H8-104553,A) to add S compound of -2 values, such as FeS, to make S concentration in slag more than 0.20wt% by entrainment churning of inactive gas, and to prevent elution of Cr6+.

[0006] (3) An elution prevention method of Cr6+ from the chromium-ores slag by which it is generated in the case of manufacture of the chromium compound which carries out reduction **** of the chromium-ores slag, returns to Cr3+ and detoxicates Cr6+.

(4) A generation prevention method of Cr6+ of the sludge incinerated ash which controls the excess air ratio at the time of incineration to less than one [A sewerage association magazine, vol.38 No.378, pp29-32 (1994)] . However, after performing reduction processing or incineration processing by the method etc. which described above the above-mentioned quality of a chromium oxidation thing inclusion, when reusing to a roadbed material, engineering-works reclamation material, temporary material, etc., after inspecting whether the chromium oxidation thing was fully returned, ship, but. When the unreturned chromium oxidation thing is sometimes mixing, the reuse to a roadbed material, engineering-works reclamation material, temporary material, etc. becomes impossible.

[0007]

[Problem to be solved by the invention] The stainless steel slag which this invention solves the problem of the above mentioned conventional technology, and is generated in the case of refinement of stainless steel, The chromium-ores slag by which it is generated in the case of manufacture of chromium compounds, such as potassium sodium, Industrial waste molten slag, The disposal method of the quality of a chromium oxidation thing inclusion which can prevent elution of Cr6+ from quality of a chromium oxidation thing inclusion, such as slag adherence refractories used for refinement of a sewage sludge and stainless steel, the utilizing method of the quality of a chromium oxidation thing inclusion using it and a roadbed material, engineering-works reclamation material, It aims at providing temporary material.

[0008]

[Means for solving problem] As a result of examining the problem of the above mentioned conventional technology wholeheartedly, this invention persons by specified-quantity-adding sulfur content slag in the quality of a chromium oxidation thing inclusion after reduction processing, and mixing in it, Elution of Cr6+ from the quality of a chromium oxidation thing inclusion was prevented thoroughly, and it found out that it was possible to use effectively as a roadbed material, engineering-works reclamation material, temporary material, etc.

[0009] That is, the 1st invention is the quality 100 of a chromium oxidation thing inclusion after reduction processing. It is a disposal method of the quality of a chromium oxidation thing inclusion 0.1---90-weight-section-adding sulfur content slag, and mixing to a weight section. The 2nd invention sulfur content slag to

nature of chromium oxidation thing inclusion 100 weight section after reduction processing 0.1 - 90 weight-section addition, After mixing, it is a utilizing method of the quality of a chromium oxidation thing inclusion characterized for the obtained mixture by the thing of a roadbed material, engineering-works reclamation material, and temporary material used for either at least.

[0010]The 3rd invention is the quality 100 of a chromium oxidation thing inclusion after reduction processing. It is a roadbed material characterized by being 0.1---90-weight-section-added and coming to mix sulfur content slag to a weight section. The 4th invention is the quality 100 of a chromium oxidation thing inclusion after reduction processing. It is the engineering-works reclamation material characterized by being 0.1---90-weight-section-added and coming to mix sulfur content slag to a weight section.

[0011]The 5th invention is the quality 100 of a chromium oxidation thing inclusion after reduction processing. It is the temporary material characterized by being 0.1---90-weight-section-added and coming to mix sulfur content slag to a weight section.

[0012]

[Mode for carrying out the invention]Hereafter, this invention is explained still in detail. As the reduction method of the quality of a chromium oxidation thing inclusion in this invention, If it is the method of returning Cr6+ in the quality of a chromium oxidation thing inclusion, restriction in particular will not be carried out, but it is preferred that it is the reduction method that the Cr6+ elution volume by the elution test method by the Environment-Protection-Agency notifying No. 46 method can attain 0.05 or less mg/l.

[0013]Although it is possible to use the above mentioned conventional method as such a reduction method, it is following (1) as a more desirable method. The method of - (6) is mentioned.

(1) How to make the solution in which sulfur and/or the oxidation number contain the compound of sulfur below +5 value 0.05weight % or more contact the quality of a chromium oxidation thing inclusion.

(2) How to mix the quality of a chromium oxidation thing inclusion, and unaged shaft furnace slow cooling slag, and settle out in the fields.

[0014](3) How to water the quality of a chromium oxidation thing inclusion in the blast-furnace-slag eluted water generated at the time of watering cooling of blast furnace slag.

(4) How to immerse the quality of a chromium oxidation thing inclusion in the blast-furnace-slag eluted water generated at the time of watering cooling of blast furnace slag.

(5) How to water the blast-furnace-slag eluted water which mixes the quality of a chromium oxidation thing inclusion, and unaged shaft furnace slow cooling slag, and is generated into this mixture at the time of watering cooling of water and/or blast furnace slag.

[0015](6) How to mix the quality of a chromium oxidation thing inclusion, and unaged shaft furnace slow cooling slag, and blow a steam into this mixture.

In this invention, after carrying out reduction processing of the quality of a chromium oxidation thing inclusion by the above-mentioned method etc., sulfur content slag is added in the obtained quality of a chromium oxidation thing inclusion, and it mixes in it. According to this invention, elution of Cr6+ from the quality of a chromium oxidation thing inclusion was prevented thoroughly, and the above-mentioned processing enabled it to use effectively as a roadbed material, engineering-works reclamation material, temporary material, etc.

[0016]As sulfur content slag in this invention, sulfur content slag, such as slag which mixed the shaft furnace slow cooling slag after aging, molten iron conditioning slag, or these, is illustrated preferably. The addition of the sulfur content slag to the quality of a chromium oxidation thing inclusion after reduction processing is the quality 100 of a chromium oxidation thing inclusion

after reduction processing. It is preferred to carry out 0.1 -90 weight-section addition of the sulfur content slag to a weight section.

[0017]the addition of sulfur content slag -- 0.1 -- when it is less than a weight section, perfect prevention of elution of Cr6+ from the quality of a chromium oxidation thing inclusion becomes difficult -- reverse -- 90 weight copy -- when obtaining more than, it is not economical from fields, such as necessary energy which the amount of handling of sulfur content slag increases, and mixing takes. the sulfur content of the sulfur content slag in this invention -- the total quantity of simple substance sulfur and sulfur in sulfur compounds -- 0.2 -- it is preferred that it is more than weight % -- more -- desirable -- simple substance sulfur and the oxidation number -- the total quantity of sulfur below +5 value -- 0.1 -- it is preferred that it is more than weight %.

[0018]By adding sulfur content slag in the quality of a chromium oxidation thing inclusion after reduction processing, and mixing in it, as a Reason for the ability to prevent thoroughly elution of Cr6+ from the quality of a chromium oxidation thing inclusion, the sulfur component which exists in sulfur content slag elutes underwater, and it thinks for returning Cr6+. Namely, S0 in sulfur content slag, such as shaft furnace slow cooling slag after aging and molten iron conditioning slag, S2O32-, and SO42- dissolve in water, Among those, when S0 and S2O32- oxidize to SO42 - , it is thought that Cr6+ is returned.

[0019]According to this invention, since sulfur content slag returns chromium and considers it as the form of stable chromium, such as Cr(OH) 3, by contacting the quality of a chromium oxidation thing inclusion under existence of moisture, elution of the chromium oxidation thing from the quality of a chromium oxidation thing inclusion can be prevented thoroughly. In this invention, it is also possible to use together other reducing agents, such as ferrous sulfate with the operation which returns a chromium oxidation thing in addition to sulfur content slag, and activated carbon.

[0020]

[Working example]Hereafter, this invention is concretely explained based on an embodiment. The Cr6+ elution volume in this example was measured based on the elution test method by the Environment-Protection-Agency notifying No. 46 method.

(Comparative examples 1 and 2) As quality of a chromium oxidation thing inclusion, (1) stainless-steel slag and (2) stainless-steel refinement slag adherence refractories were used.

[0021]Stainless steel slag is the sample sampled in reduction down stream processing in the middle of refinement. The Cr6+ elution volume of such quality of a chromium oxidation thing inclusion is shown below.

(1) Stainless steel slag : 10.5 mg/l (2) stainless steel refinement slag adherence refractories: Reduction processing was performed by the method (C, D) of showing the quality of a chromium oxidation thing inclusion which carried out the 0.12 mg/l above in Table 1.

[0022]The Cr6+ elution volume in the sample after reduction processing combines the incidence rate (: reject ratio) exceeding 0.05 mg/l of a sample with a reduction disposal method, and shows it in Table 2. As shown in Table 2, the incidence rate of the sample to which the Cr6+ elution volume in the stainless steel slag after reduction processing and the sample of stainless steel refinement slag adherence refractories exceeds 0.05 mg/l was 0.10%.

[0023](Comparative examples 3-6) the stainless steel slag same as quality of a chromium oxidation thing inclusion as having used by said comparative examples 1 and 2 carried out, and stainless steel refinement slag adherence refractories -- in addition, chromium-ores slag and sewage-sludge molten slag were used. A Cr6+ elution volume of such quality of a chromium oxidation thing inclusion is shown below.

[0024]

(1) Chromium-ores slag : 25.3 mg/l (2) sewage-sludge molten slag : Reduction

processing was performed by a method (B, C, D) of showing quality of a chromium oxidation thing inclusion which carried out the 0.80 mg/l above in Table 1. as opposed to nature of chromium oxidation thing inclusion 100 weight section after reduction processing -- shaft furnace slow cooling slag after aging, and molten iron conditioning slag -- 0.05 -- it 0.09-weight-sections-added and mixed.

[0025]In the total quantity of simple substance sulfur and sulfur in sulfur compounds, simple substance sulfur and the oxidation number was [the total quantity of sulfur below +5 value of a sulfur content of shaft furnace slow cooling slag after used aging] 0.42 weight % 0.85weight %. In the total quantity of simple substance sulfur and sulfur in sulfur compounds, simple substance sulfur and the oxidation number was [the total quantity of sulfur below +5 value of a sulfur content of molten iron conditioning slag] 0.12 weight % 0.40weight %.

[0026]A Cr6+ elution volume in a sample of obtained various mixtures combines an incidence rate (: a reject ratio) of a sample which exceeds 1. in 0.05mg /with a kind of a reduction disposal method and sulfur content slag added and mixed, and an addition, and shows it in Table 2. As shown in Table 2, an addition of sulfur content slag to nature of chromium oxidation thing inclusion 100 weight section after reduction processing is 0.1. When it was less than a weight section, an incidence rate of a sample to which a Cr6+ elution volume exceeds 0.05 mg/l was 0.05%.

[0027](Embodiment 1) Reduction processing was performed by a method (C) of showing the same stainless steel slag in Table 1 with having used by the comparative example 1. It is shaft furnace slow cooling slag after aging to stainless steel slag 100 weight section after reduction processing 0.1 It weight-section-added and mixed.

[0028]In the total quantity of simple substance sulfur and sulfur in sulfur compounds, simple substance sulfur and the oxidation number was [the total quantity of sulfur below +5 value of a sulfur content of shaft furnace slow cooling slag after used aging] 0.42 weight % 0.85weight %. An incidence rate of a sample to which a Cr6+ elution volume in a sample of an obtained mixture exceeds 1. in 0.05mg /was 0.00%.

[0029](Embodiments 2-24) As quality of a chromium oxidation thing inclusion, (1) stainless-steel refinement slag, (2) stainless-steel refinement slag adherence refractories, (3) chromium-ores slag, and (4) sewage-sludge molten slag were used. A Cr6+ elution volume of such quality of a chromium oxidation thing inclusion is shown below.

(1) Stainless steel refinement slag : 10.5 mg/l (2) stainless steel refinement slag adherence refractories: 0.12 mg/l (3) chromium-ores slag : 25.3 mg/l (4) sewage-sludge molten slag : Various quality of a chromium oxidation thing inclusion which carried out the 0.80 mg/l above. It is the quality 100 of a chromium oxidation thing inclusion with a method (A, B, C, D) shown in Table 1 about shaft furnace slow cooling slag after reduction processing and aging, and molten iron conditioning slag. To a weight section, it 0.1---90-weight-section-added and mixed.

[0030]In the total quantity of simple substance sulfur and sulfur in sulfur compounds, simple substance sulfur and the oxidation number was [the total quantity of sulfur below +5 value of the sulfur content of the shaft furnace slow cooling slag after used aging] 0.42 weight % 0.85weight %. In the total quantity of simple substance sulfur and sulfur in sulfur compounds, simple substance sulfur and the oxidation number was [the total quantity of sulfur below +5 value of the sulfur content of molten iron conditioning slag] 0.12 weight % 0.40weight %.

[0031]The Cr6+ elution volume in the sample of the obtained various mixtures combines the incidence rate (: reject ratio) of a sample which exceeds 1. in 0.05mg /with the kind of a reduction disposal method and sulfur content slag added and mixed, and an addition, and shows it in Table 2. The incidence rate of the sample to which a Cr6+ elution volume exceeds 0.05 mg/l according to the

method of this invention as shown in Table 2, That is, the reject ratio of the inspection before shipment for shipping as a roadbed material, engineering-works reclamation material, temporary material, etc. was understood that it can fall to 0.00% from conventional 0.05 to 0.10%.

[0032] Although unaged shaft furnace slow cooling slag and blast-furnace-slag eluted water were used for addition of sulfur content slag, and reduction processing of the quality of a chromium oxidation thing inclusion before mixing in this example, in this invention, the reduction disposal method in particular of this quality of a chromium oxidation thing inclusion is not restricted.

[0033]

[Table 1]

| | 硫黄含有スラグ添加、混合に先立つ還元処理方法 |
|---|--|
| A | 未エージング高炉徐冷スラグを添加、混合後、散水 |
| B | 高炉スラグの散水冷却時に発生する高炉スラグ溶出水中に1週間浸漬 |
| C | 未エージング高炉徐冷スラグを添加、混合後、100℃の水蒸気を24時間吹き込み |
| D | 高炉スラグの散水冷却時に発生する高炉スラグ溶出水を散水 |

[0034]

[Table 2]

【表2-1】

| | 処理対象物質 | 硫黄含有スラグ添加、混合に先立つ還元処理方法 * | 添加、混合した硫黄含有スラグ | | 不合格率 *** (%) |
|------|----------------|-----------------------------|----------------|-----------------|--------------------|
| | 種類 | | 種類 | 添加量 ** (重量部) | |
| 比較例1 | ステンレス鋼スラグ | C | 未添加 | 0 | 0.10 |
| 比較例2 | ステンレス鋼スラグ付着耐火物 | D | 未添加 | 0 | 0.10 |
| 比較例3 | ステンレス鋼スラグ | C | エージング後の高炉徐冷スラグ | 0.05 | 0.05 |
| 比較例4 | ステンレス鋼スラグ付着耐火物 | D | 溶銑予備処理スラグ | 0.09 | 0.05 |
| 比較例5 | クロム鉍滓 | C | エージング後の高炉徐冷スラグ | 0.05 | 0.05 |
| 比較例6 | 下水汚泥溶融スラグ | B | 溶銑予備処理スラグ | 0.09 | 0.05 |
| 実施例1 | ステンレス鋼スラグ | C | エージング後の高炉徐冷スラグ | 0.1 | 0.00 |
| 実施例2 | ステンレス鋼スラグ付着耐火物 | D | 溶銑予備処理スラグ | 0.1 | 0.00 |
| 実施例3 | クロム鉍滓 | C | エージング後の高炉徐冷スラグ | 0.1 | 0.00 |
| 実施例4 | 下水汚泥溶融スラグ | B | 溶銑予備処理スラグ | 0.1 | 0.00 |
| 実施例5 | ステンレス鋼スラグ | D | エージング後の高炉徐冷スラグ | 5.0 | 0.00 |
| 実施例6 | ステンレス鋼スラグ付着耐火物 | D | 溶銑予備処理スラグ | 5.0 | 0.00 |
| 実施例7 | クロム鉍滓 | D | エージング後の高炉徐冷スラグ | 5.0 | 0.00 |
| 実施例8 | 下水汚泥溶融スラグ | D | 溶銑予備処理スラグ | 5.0 | 0.00 |

備考) †: 記号は表1の還元処理方法を示す。

** : 還元処理後のクロム酸化物含有物質100重量部に対する重量部を示す。

***: 硫黄含有スラグ添加、混合後のサンプルにおける、Cr⁶⁺溶出量が0.05mg/lを超えるサンプルの発生率。

[0035]

[Table 3]

【表 2-2】

| | 処理対象物質 | 硫黄含有スラグ添加、混合に先立つ還元処理方法 * | 添加、混合した硫黄含有スラグ | | 不合格率 *** (%) |
|-------|----------------|-----------------------------|----------------|-----------------|--------------------|
| | 種 類 | | 種 類 | 添加量 ** (重量部) | |
| 実施例 9 | ステンレス鋼スラグ | B | エージング後の高炉徐冷スラグ | 0.1 | 0.00 |
| 実施例10 | ステンレス鋼スラグ付着耐火物 | B | 溶銑予備処理スラグ | 0.1 | 0.00 |
| 実施例11 | クロム鉱滓 | B | エージング後の高炉徐冷スラグ | 0.1 | 0.00 |
| 実施例12 | 下水汚泥熔融スラグ | A | 溶銑予備処理スラグ | 0.1 | 0.00 |
| 実施例13 | ステンレス鋼スラグ | B | エージング後の高炉徐冷スラグ | 5.0 | 0.00 |
| 実施例14 | ステンレス鋼スラグ付着耐火物 | B | 溶銑予備処理スラグ | 5.0 | 0.00 |
| 実施例15 | クロム鉱滓 | B | エージング後の高炉徐冷スラグ | 5.0 | 0.00 |
| 実施例16 | 下水汚泥熔融スラグ | B | 溶銑予備処理スラグ | 5.0 | 0.00 |
| 実施例17 | ステンレス鋼スラグ | C | エージング後の高炉徐冷スラグ | 2.0 | 0.00 |
| 実施例18 | ステンレス鋼スラグ付着耐火物 | C | 溶銑予備処理スラグ | 2.0 | 0.00 |
| 実施例19 | クロム鉱滓 | C | エージング後の高炉徐冷スラグ | 2.0 | 0.00 |
| 実施例20 | 下水汚泥熔融スラグ | C | 溶銑予備処理スラグ | 2.0 | 0.00 |
| 実施例21 | ステンレス鋼スラグ | C | 溶銑予備処理スラグ | 90 | 0.00 |
| 実施例22 | ステンレス鋼スラグ付着耐火物 | B | 溶銑予備処理スラグ | 90 | 0.00 |
| 実施例23 | クロム鉱滓 | C | エージング後の高炉徐冷スラグ | 90 | 0.00 |
| 実施例24 | 下水汚泥熔融スラグ | A | エージング後の高炉徐冷スラグ | 90 | 0.00 |

備考) *: 記号は表 1 の還元処理方法を示す。

**: 還元処理後のクロム酸化物含有物質100 重量部に対する重量部を示す。

***: 硫黄含有スラグ添加、混合後のサンプルにおける、 Cr^{6+} 溶出量が 0.05mg/l を超えるサンプルの発生率。

[0036]

[Effect of the Invention] By this invention, waste molten slag, such as stainless steel slag, chromium-ores slag, and sewage-sludge molten slag, It became possible to prevent thoroughly elution of Cr^{6+} from quality of a chromium oxidation thing inclusion, such as slag adherence refractories used for refinement of stainless steel, and it became possible to perform easily reuse to the roadbed material of the quality of a chromium oxidation thing inclusion, engineering-works reclamation material, temporary material, etc.